Micro scale Isotope Variations in Terrestrial Carbonates as Biomarkers: Analogs for Martian Processes

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Understanding the isotopic geochemistry of terrestrial carbonate formation is essential to understanding the evolution of the Martian atmosphere, hydrosphere, and potential biosphere. Carbonates are important secondary minerals for interpreting past aqueous environments, as illustrated by those in ALH84001. A thorough understanding of the effects of aqueous weathering and potential contribution of organic compounds on the isotopic composition of Martian carbonates can be gained by studying some terrestrial occurrences of carbonate rocks.

We have undertaken a study of micro scale stable isotope variations measured in some terrestrial carbonates and the influence of organic compounds associated with the formation of these carbonates. Preliminary results indicate that isotope variations occur within narrow and discrete intervals, providing clues to paleo-environmental conditions that include both biological and non-biological activity. These results carry implications for deciphering Martian isotope data and therefore potential biological prospecting on the planet Mars. Recently, Mars Express has detected methane occurring in the Martian atmosphere that could be attributed to a possible biogenic source. Indeed, calcite formed from the oxidation of organic material (i.e., methane in soil gas) is typically strongly depleted in ¹³C owing to the influence of the source hydrocarbon, formed principally by:

- (1) Aerobic: $CH_4+2O_2+Ca^{2+}=CaCO_3+H_2O+2H^+$, and
- (2) Anaerobic: $CH_4+SO_4^{-2}+Ca^{2+}=CaCO_3+H_2S+H_2O$.

 $\delta^{18}O_{(PDB)}$ and $\delta^{13}C_{(PDB)}$ analyses of micro milled growth layers in "teskel" zone caliche collected from NW Yucatan, range from -4.54 to -1.21‰, and -10.84 to +1.27‰, respectively. Variations in ^{13}C imply alteration within the vadose zone, with ^{13}C -depletions attributed to light soil gas CO_2 derived from oxidation of organic matter by either reaction (1) or (2), and ^{13}C enrichments attributed to subaerial exposure during precipitation. O isotope variations are indicative of meteoric diagenesis with ^{18}O enrichments due to evaporation effects, and ^{18}O depletions due either to sulfate reduction (reaction 2), or the influence of ^{18}O -depleted meteoric precipitation (tropical cyclones).

Additional material for this study was collected from thermal springs in N. Nevada. $\delta^{13}C_{(PDB)}$ composition of CO_2 /methane gas mixtures range from -4.9 to -23.6%, and -23.7 to -71.9%, respectively. These variations could indicate a biogenic vs. thermogenic source for methane that may be imprinted on the $\delta^{13}C$ of the solid carbonate.

This work provides valuable information for better understanding the processes that control organically influenced carbonate mineral precipitation, which will allow us to better decipher data collected from Martian carbonates.